



MW: 100.12

CAS: 80-62-6

RTECS: OZ5075000

METHOD: 2537, Issue 2

EVALUATION: FULL

Issue 1: 15 May 1989

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OSHA : 100 ppm  
 NIOSH: 100 ppm  
 ACGIH: 100 ppm  
 (1 ppm = 4.10 mg/m<sup>3</sup> @ NTP)

PROPERTIES: liquid; d 0.944 g/mL @ 20 °C;  
 BP 100 °C; VP 4.7 kPa (35 mm Hg)  
 @ 20 °C; explosive range 1.7 to 8.2% v/v  
 in air

SYNONYMS: methacrylic acid methyl ester.

| SAMPLING  |   | MEASUREMENT                                |  |
|---|---|--|--|
| <b>SAMPLER:</b>                                       | SOLID SORBENT TUBE<br>(XAD-2, 400 mg/200 mg)      | <b>TECHNIQUE:</b>                          | GAS CHROMATOGRAPHY, FID                                      |
| <b>FLOW RATE:</b>                                     | 0.01 to 0.05 L/min                                | <b>ANALYTE:</b>                            | methyl methacrylate  |
| <b>VOL-MIN:</b>                                       | 1 L @ 100 ppm                                     | <b>DESORPTION:</b>                         | 2 mL CS <sub>2</sub> ; stand 30 min                          |
| <b>-MAX:</b>  | 8 L   | <b>INJECTION VOLUME:</b>                   | 1 µL   |
| <b>SHIPMENT:</b>                                      | in dry ice  | <b>TEMPERATURE-INJECTION:</b>              | 250 °C   |
| <b>SAMPLE STABILITY:</b>                              | ≥ 7 days @ 25 °C [1];<br>≥ 32 days @ 4 °C [2]     | <b>-DETECTOR:</b>                          | 300 °C   |
| <b>BLANKS:</b>  | 2 to 10 field blanks per set                      | <b>-COLUMN:</b>                            | 100 °C   |
| <b>ACCURACY</b>                                       |   | <b>CARRIER GAS:</b>                        | He, 1 mL/min, makeup 20 mL/min                               |
| <b>RANGE STUDIED:</b>                                 | 193 to 725 mg/m <sup>3</sup><br>(3-L samples) [3] | <b>COLUMN:</b>                             | 30 m x 0.25-mm ID DB-1; 1-µm film fused silica capillary [2] |
| <b>BIAS:</b>  | 2.55%   | <b>CALIBRATION:</b>                        | standard solutions of methyl methacrylate in CS <sub>2</sub> |
| <b>OVERALL PRECISION (<math>\hat{S}_{rT}</math>):</b> | 0.063 [3]   | <b>RANGE:</b>                              | 0.03 to 1 mg per sample [2,3]                                |
| <b>ACCURACY:</b>                                      | ± 12.6%   | <b>ESTIMATED LOD:</b>                      | 0.01 mg per sample [2]                                       |
|   |   | <b>PRECISION (<math>\hat{S}_p</math>):</b> | 0.007 @ .56 to 2.35 mg per sample [1]                        |

**APPLICABILITY:** The working range is 2.4 to 270 ppm (10 to 1100 mg/m<sup>3</sup>) for a 3-L air sample. Because of the similarity in the chemical structures and properties of methyl methacrylate and ethyl methacrylate and the available stability and desorpt ion efficiency data this method may also be useful for determining ethyl methacrylate in air [4].

**INTERFERENCES:** None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

**OTHER METHODS:** This revises NIOSH Method S43 [5], which utilized a 20-ft x 1/8-inch stainless steel column, packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport with nitrogen as carrier gas at 30 mL/min.

**REAGENTS:**

1. Methyl methacrylate, chromatographic quality.
2. Carbon disulfide, reagent grade.\*
3. Undecane, 99%
4. Eluent: carbon disulfide, containing 0.1% (v/v) undecane or other suitable internal standard.
5. Calibration stock solution, 94.4 mg/mL. Dilute 10.0 mL methyl methacrylate to 10 mL with eluent.
6. Helium, prepurified.
7. Hydrogen, prepurified.
8. Air, filtered, compressed.

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections (front = 400 mg; back = 200 mg) of XAD-2 resin (20/50 mesh), contained and separated by plugs of silylated glass wool. Tubes are commercially available (SKC, ST 226-30-06 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (see page 2537-1).
4. Syringes, microliter, 10- $\mu$ L, readable to 0.1  $\mu$ L.
5. Pipets, various sizes to prepare standards.
6. Flasks, volumetric, 10-mL.
7. Vials, 2- and 5-mL, glass with PTFE-lined screw caps.

**SPECIAL PRECAUTIONS:** Carbon disulfide is toxic and a serious fire and explosion hazard (has flash point = -30 °C); work with it only in a hood. Methyl methacrylate may cause irritation of the nose, throat, skin and eyes [6].

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at a known flow rate between 0.01 to 0.05 L/min for a sample size of 1 to 8 L.
4. Cap the samplers. Pack securely for shipment in a cold container at 4 °C or lower.

**SAMPLE PREPARATION:**

5. Place the front and back sorbent sections in separate 5-mL vials. Discard plugs.
6. Add 2.0 mL eluent to each vial. Cap each vial.
7. Allow to stand 30 min. with occasional agitation.

**CALIBRATION AND QUALITY CONTROL:**

8. Calibrate daily with at least six working standards.
  - a. Add known amounts of analyte or calibration stock solution to eluent in 10-mL volumetric flasks and dilute to mark. Use serial dilutions as needed to obtain methyl methacrylate concentrations in the range 0.005 to 0.5 mg/mL.
  - b. Analyze together with samples and blanks (steps 11 and 12).
  - c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of XAD-2 used. Prepare three tubes at each of five levels plus three media blanks.
  - a. Remove and discard back sorbent section of media blank samplers.
  - b. Inject a known amount (2 to 20  $\mu$ L) of calibration stock solution directly into front sorbent section with a microliter syringe.
  - c. Cap the tubes and allow to stand overnight.
  - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).

- e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

**MEASUREMENT:**

11. Set gas chromatograph according to manufacturer's recommendations and to condition given on page 2537-1. Inject sample aliquot manually using solvent flush technique or with an autosampler.
12. Measure peak area. Divide the peak area of the analyte by the peak area of the internal standard on the same chromatogram.

**CALCULATIONS:**

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front ( $W_f$ ) and back ( $W_b$ ) sorbent sections, and in the average media blank front ( $B_f$ ) and back ( $B_b$ ) sorbent sections. NOTE: If  $W_b \geq W_f/10$ , report breakthrough and possible sample loss.
14. Calculate concentration, C, of methyl methacrylate in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

**EVALUATION OF METHOD:**

Method S43 was issued on July 6, 1979, and validated with generated atmospheres over the concentration range 193 to 725 mg/m<sup>3</sup> [3,7]. Average recovery was 98.1% (18 samples) in the range 0.56 to 2.35 mg/sample. Overall precision ( $\hat{S}_{rT}$ ) was estimated to be 0.063. Breakthrough volume was 6.46 L for 786 mg/m<sup>3</sup> methyl methacrylate in air with 90% relative humidity. In order to achieve greater sensitivity, analytical modifications in the method were made [2]. Desorption efficiency was checked by spiking 0.56 to 2.4 mg per sample onto XAD-2 tube; DE found was in the range 0.96 to 1.0. Storage studies over 32 days at 4 °C showed an average recovery of 97.3% [2].

A storage and stability study for ethyl methacrylate was performed on XAD-2 using 0.14 to 1.4 mg of analyte per sample at 20 °C and also at 4 °C for 23 days. The results of the study indicated an average recovery in the range 95 to 10% [4].

**REFERENCES:**

- [1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare Publ. (NIOSH) 77-185 (1977).
- [2] Tanguay, James F., Method Modification Efforts for Methyl Methacrylate, NIOSH, DPSE, MRSB, (unpublished, 1988).
- [3] Backup Data Report for Methyl Methacrylate, S43, prepared under NIOSH Contract 210-76-0123 (1979).
- [4] Tanguay, James F., Method Development Efforts for Ethyl Methacrylate, NIOSH, DPSE, MRSB, (unpublished, 1989).
- [5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, S43, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-125 (1980).
- [6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
- [7] NIOSH Research Report Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services Publ. (NIOSH) 80-133 (1980).

**METHOD REVISED BY:**

Robert W. Kurimo, NIOSH/DPSE; S43 originally validated under NIOSH Contract No. 210-76-0123.